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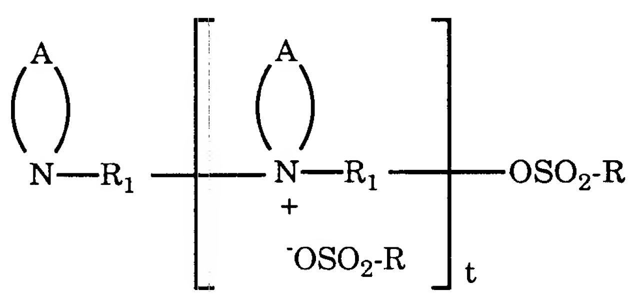
(71) Applicant: **ROHM AND HAAS COMPANY**
Independence Mall West
Philadelphia Pennsylvania 19105(US)

(72) Inventor: **Sherba, Samuel Eugene**
41 Mont Claire Lane
Willingboro, New Jersey 08046(US)
Inventor: **Hsu, Adam Chi-Tung**
1686 Heebner Way
Lansdale, Pennsylvania 194466(US)
Inventor: **Mehta, Raj J.**
684 General Scott Road
King of Prussia, Pennsylvania 19406(US)
Inventor: **Bowers-Daines, Margaret Marie**
107 North Stone Ridge Drive
Lansdale, Pennsylvania 19446(US)

(74) Representative: **Smith, Julian Philip Howard et al**
Rohm and Haas (UK) Limited, European Operations Patent Dept., Lennig House, 2 Masons Avenue
Croydon CR9 3NB(GB)

(54) Antimicrobial polymeric quaternary ammonium salts.

(57) Compounds of the formula



(V)

wherein R is (C_1-C_{20})alkyl, (C_1-C_{20})cycloalkyl, or (C_6-C_{20})aryl, aralkyl or alkaryl each optionally substituted on the aryl portion with one or more of halo, nitro, (C_1-C_4)alkyl, or cyano;

A is $(CH_2)_p$, $(CH_2)_q$-O-$(CH_2)_r$, or $(CH_2)_q$-S-$(CH_2)_r$,

wherein p = 2 to 8, q = 1 to 8, and r = 1 to 8;

R_1 = -$(CH_2)_m$-, -$(CH_2CH_2$-O$)_n$-CH_2CH_2-, or -$(CH_2CH_2CH_2$-O$)_n$-$CH_2CH_2CH_2$- where m is from 7 to 24 and n is from 1 to 10; and t is from 1 to 100

are disclosed, as are monomers of the formula

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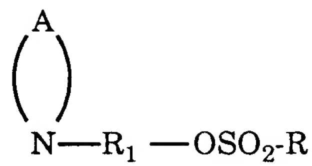


(IV)

The polymers have microbicidal activity.

This invention concerns the control of microorganisms, and more particularly concerns control using novel polymeric quaternary ammonium salts.

The self-condensation of various bromoalkylamines has been studied since 1906 starting with bromoethyldimethylamine which reacted with itself to form a cyclic quat with a 6-membered ring, reported by Knorr and Roth, Ber., 39, 1425(1906).

Kern and Brenneisen, J. Prakt. Chem., 159, 193 (1941), reported another type of linear polyquat using di-tertiary amines to react with di-halides. Both starting materials are readily available.

Carothers, JACS, 51, 2548 (1929) suggested a polymeric quat from bromoalkylamines.

Marvel et al., JACS, 49,2299 (1927) suggested intracyclization of bromobutyldimethylamine to form cyclic quats. Other reports by Marvel and colleagues were published in JACS, 52, 287 (1930), JACS, 55, 753 (1933), JACS, 55, 1977 (1933), JACS, 56, 725 (1934), and JACS, 57, 1127 (1935).

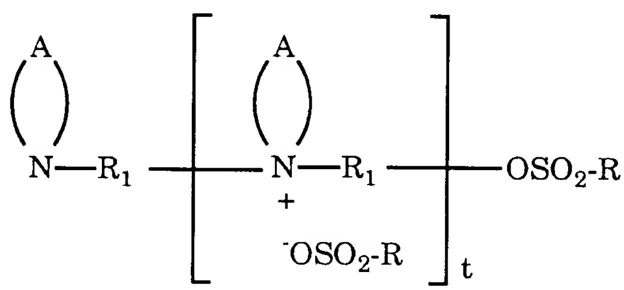
Ritter, U.S.-A-2,261,002 and Searle et al, U.S.-A-2,271,378, both assigned to Dupont, disclosed polymeric quats having pesticidal utility (fungicides, insecticides, disinfectants).

Rembaum, et al, Polymer Letters, 6, 159 (1968), named both type polyquats as "aliphatic ionenes."

Noguchi, et al, Poly. Prepr. ACS Dev. Polym. Chem., 10, 718 (1969) reviewed cyclic, linear and polymeric ammonium salts.

Bortel et al, published studies on "Chloro-ionenes"; "Chloro-Ionenes with Ether Bonds in the Backbone Chain. Determination of Rate Constants, Orders of Reaction and Molecular Weights," Makromol. Chem., 182, 3099-3108 (1981), and "Chloro-Ionenes from Dichlorides and tertiary diamines," Makromol. Chem., 188, 2019 (1987).

We have discovered certain novel quaternary ammonium salts and polymers thereof, the polymers having microbicidal activity. Accordingly in one aspect the present invention provides compounds of the formula (V)



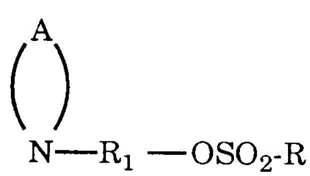
(V)

wherein R is (C_1-C_{20})alkyl, (C_1-C_{20})cycloalkyl, or (C_6-C_{20})aryl, aralkyl or alkaryl each optionally substituted on the aryl portion with one or more of halo, nitro, (C_1-C_4)alkyl, or cyano;

A is $(CH_2)_p$, $(CH_2)_q$-O-$(CH_2)_r$, or $(CH_2)_q$-S-$(CH_2)_r$,
wherein p = 2 to 8, q = 1 to 8, and r = 1 to 8;

R_1 = -$(CH_2)_m$-, -$(CH_2CH_2$-O$)_n$-CH_2CH_2-, or -$(CH_2CH_2CH_2$-O$)_n$-$CH_2CH_2CH_2$- where m is from 7 to 24 and n is from 1 to 10; and
t is from 1 to 100.

In a further aspect there are provided compounds of the formula (IV)



(IV)

wherein A, R, and R_1 are as defined above.

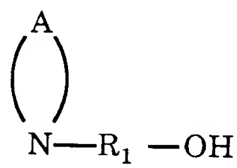
The invention also encompasses a process for producing a compound of the formula (IV) as defined above, comprising reacting a monoalcohol of the formula

X-R_1-OH (I)

wherein R_1 = $-(CH_2)_m-$, $-(CH_2CH_2-O)_n-CH_2CH_2-$, or $-(CH_2CH_2CH_2-O)_n-CH_2CH_2CH_2-$ in which m = 7 to 24, n = 1 to 10, and wherein X is a leaving group, preferably being Br, Cl, or OSO_2R in which R is alkyl, cycloalkyl, aryl, substituted aryl, alkaryl or aralkyl, with a molar excess of secondary ring amine of the formula

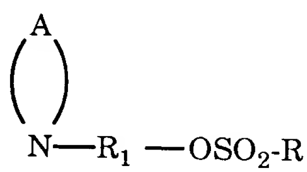
(II)

wherein A is as defined above, to form a compound of the formula



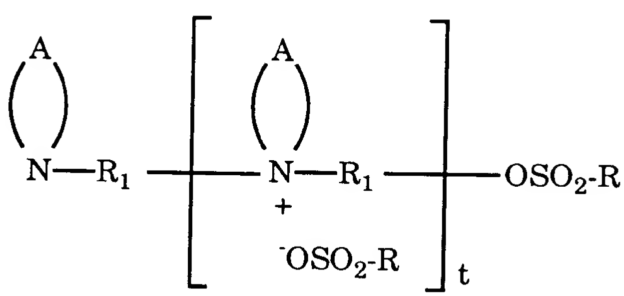
(III)

and reacting (III) with $X'SO_2R$ wherein R is as defined above and wherein X' is Cl or Br, to produce a monomer of the formula



(IV)

The monomer (IV) produced as above may be polymerized to produce a polymer of the formula



(V)

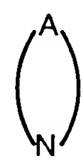
wherein t is from 1 to 100.

It will be clear to one skilled in the art that the desired chain length of the polymer (V) will be related to the length of time the monomer is allowed to polymerize. Shorter polymerization times will result in shorter chain lengths while longer polymerization times will result in longer chain lengths. Additionally, diluting the sample in an appropriate solvent or cooling the sample will slow down the polymerization, providing easier access to shorter chain length polymers; while heating the sample will decrease the amount of time necessary for complete polymerization.

A further aspect of the invention comprises a method of preventing or inhibiting the growth of bacteria, fungi or algae in a locus susceptible or subject to contamination thereby, comprising incorporating into or onto the locus, in an amount effective to adversely affect said growth, a compound or composition as

defined above. Materials which may be thus protected include wood, paint, adhesives, glue, paper, textiles, leather, plastics, cardboard, lubricants, cosmetics, food, caulking, feed and industrial cooling water.

The compounds of the invention are of formulae IV and V as set forth above. The more preferred embodiments are the polymers of formula V wherein R_1 is $-(CH_2)_m-$ where m is 11 or 12, R is p-toluene, A = $(CH_2)_p$, wherein p = 4, 5, or 6 and t = about 4 to 10.



is preferably piperidine, pyrrolidine, or hexamethyleneimine.

The polymer and monomer compounds are especially useful for controlling plant pathogenic microbes whilst having only low toxicity towards the plant. An especially effective use is against the plant pathogen of the genus *xanthomonas.*

The polymers of formula V can also be used in topical sprays for example along with an adjuvant, for example EDTA or sodium dodecyl alcohol.

As stated above, compositions comprising a polymer according to formula V and either an agronomically acceptable carrier, a cosmetic agent, a cutting oil, a soap or synthetic detergent, a stabilizer, a film forming material, or the like, have a wide range of utility for protecting against or controlling microorganisms from a wide variety of classes including fungus, bacteria, algae, viruses and yeasts. The preferred utilities of the compositions are to protect wood, paint, adhesive, glue, paper, textile, leather, plastics, cardboard, lubricants, cosmetics, food, caulking, feed and industrial cooling water from microorganisms.

The polymers of the invention are particularly valuable as microbicides in that, contrary to related commercial quat microbicides, they do not lose activity in the presence of organic matter; they are also non-corrosive to metals, and are non-foaming.

The amounts of the compound to be used depend on the application. Preferred amounts for a particular application are similar to those required for other microbicides.

The compounds can be used in combination with other microbicides. The term "microbicide" is considered equivalent to "antimicrobial" as used herein.

Suitable methods of application of compounds of formula I to control fungi, bacteria, algae, viruses, yeasts, and the like are in amounts and with carriers, etc., as well known in the art.

The following examples are presented to illustrate a few embodiments of the invention. All parts and percentages are by weight unless otherwise indicated.

The following protocol was used to evaluate biological activity:

This test is run on bacteria in synthetic hard water without the benefit of nutrients. A 1.0% slant tube is used to grow Ps.fl. which is washed with four ml of sterile water. This wash is diluted to a density of 60 to 80 NTU.

The above inoculum is diluted with SHW, 1.5 ml inoculum to 100 ml of SHW. This seeded SHW is used to fill the microtiter wells.

1. To 100 ml of sterile Synthetic Hard Water (SHW) add 1.5 ml of inoculum from the 60-80 NTU slant wash and mix well.
2. Using an 8 channel micro pipet, transfer 100 µl of the mix from a single reservoir tray to each well of the microtiter plate. Add an additional 90 µl to the first row of wells, bringing the total in row 1 to 190 µl.
3. To the top well in each column add 10 µl of compound prep, so that 6 compounds, a blank, and a standard are located along the A row. The 10 µl of 5,000 ppm prep plus 190 µl of Ps.fl. SHW make a compound concentration 250 ppm.
4. Using an 8 channel micropipet, mix and transfer 100 µl from each well of row 1 to the next row, making a 1:1 dilution to 125 ppm of the 6 compounds and standard in row 2.
5. Repeat this to make successive 1:1 dilutions to the bottom row.
6. Allow the plate to incubate for 4 hr.
7. Prepare a microtiter plate containing 100 µl TSB in each well. At one hour use the Clonemaster to transfer 5 µl from each well of the SHW plate to the TSB plate for recovering living cells.
8. Incubate this recovery plate for 24 hr. at 30°C before noting the concentration at which each

compound killed the cells in the SHW plate, resulting in clear wells or no growth in the corresponding wells of the TSB recovery plate.

A. Total Kill Test Protocol

1. Grow Psae in triptocase soy broth
2. Put 100 µl/10ml of 0.85% saline contained in 0.05 M N-tris[hydroxymethyl]methyl-2-amino ethanosulfonic acid buffer at pH 7.0.
3. Fill microtiter plates with 100 µl of #2 except top wells - they contain 190 µl of #2.
4. Add 10 µl of test compound at time zero then serial dilute by 2X.
5. Using a 96 pin (1.5 µl each pin) Dynatech inoculator recover to triptocase soy broth agar plate by touching agar with 96 pins.
6. Incubate at 30° C for 48 hours.
7. Read the pin spot where no growth occurred. This is the point that total kill occurs with a certain concentration/test compound at a certain time.

C. Speed of Kill ("SOK") tests were run as follows:

1. Grow Psae or Saur or Sal chlo on triptocase soy broth agar slants.
2. Wash slants with 10 ml 0.85% saline, 0.05 N-tris[hydroxymethyl]methyl-2-amino ethanosulfonic acid buffer pH 7.0.
3. Pour #2 into sterile vial.
4. Vortex #3.
5. Add 10 ml of #4 to sterile 2 oz jar with a stirring bar.
6. Remove 100 ml of #5 to triptocase soy broth for zero time call count.
7. Add test compound at desired concentrations.
8. With time intervals remove adjuvants to 100 ml of sterile triptocase soy broth.
9. Do cell counts of #8 by pour plating in sterile triptocase soy broth agar.
10. Incubate agar plates at 30° C for 72 hours.
11. Calculate log reduction of viable cells.

D. Minimum inhibitory concentration (MIC) values were obtained using a broth, two-fold serial dilution test performed as follows: A stock solution or dispersion of the test compound, typically at a concentration of 1%, is made in a 5:3:2 solvent solution of acetone, methanol, and water. A volume of the stock solution is dispensed into culture media to give an initial starting test concentration of 500 ppm compound.

When the test is ready to be done, each vessel in the dilution series, except the first vessel, contains an equal volume of compound free broth. The first vessel contains twice the volume of broth with the starting concentration of test compound. One half of the broth from the first vessel is transferred to the second vessel. After being mixed, one half the resulting volume is removed from the second vessel and transferred to the third vessel. The entire cycle is repeated sufficiently to give a series of concentrations amounting to 250, 125, 63, 31, 16, 8, and 4, 2, 1, 0.5, 0.25, and 0.12 ppm

Each vessel is then inoculated with a cell suspension of the appropriate test organism. Bacteria are grown in broth; fungi on agar slants for a time and at a temperature appropriate to the species being tested; and algae are a mixture of green algae and blue-green bacteria grown in a nutrient media. At the end of the growth period, in the case of bacteria, the broth is vortexed to disperse the cells.

In the case of fungi, the spores are harvested by pipetting water onto the slant and dislodging the spores with a sterile loop. The cell/spore suspension is standardized by controlling incubation time, temperature, and the volume of the diluent. The suspension is then used to inoculate the vessels containing the broth compound.

The algae culture contains green algae and blue-green bacteria, and is obtained from a cooling tower in Spring House, Pennsylvania. The algae culture is grown in Allen's medium on a rotary shaker under flourescent room lighting. This culture is further diluted with Allen's medium and then added to the test vessel.

The vessels are then incubated at the appropriate temperature. After the incubation, the vessels are examined for growth/no growth. The minimum inhibitory concentration (MIC) is defined as the lowest concentration of compound that results in complete inhibition of growth of the test organism.

The organisms tested to demonstrate microbicidal activity include:

BACTERIA:

Pseudomonas fluorescens (PSFL), gram negative

Pseudomonas aeruginosa (PSAE), gram negative
Escherichia coli (ECOL), gram negative
Staphylococcus aureus (SAUR), gram positive
FUNGI:
Aspergillus niger (ANIG)
Aureobasidium pullulans (APUL)

Example 1

A. Synthesis of 11-(N-piperidyl)undecane-1-(p-toluene)sulfonate

11-Bromoundecanol (11.00 g., 43.79 mmole) was dissolved in 100 ml. of piperidine and heated at reflux temperature for 18 hours. The reaction mixture was allowed to cool and most of the precipitated piperidine hydrobromide was removed by filtration. The excess piperidine is removed by simple distillation and the resultant solid residue is recrystallized from ethanol and water. After drying, 10.78 g. (96.3% yield) of 1-hydroxy-11-(N-piperidyl)undecane was obtained. m.p. 62-65° C, ^{1}H-NMR (200 MHz, $CDCl_3$) d = 1.2-1.7 ppm, m, 24H; 2.10, broad s, 1H; 2.20-2.45, m, 6H; 3.63, t, 2H.

The 1-Hydroxy-11-(N-piperidyl)undecane (10.70 g., 41.89 mmole) was dissolved in 200 ml. of anhydrous methylene chloride. The solution was cooled to 0° C with an ice bath and then treated with 4-(N,N-dimethylamino)pyridine (5.12 g., 41.91 mmole) followed by p-toluenesulfonyl chloride (7.99 g., 41.91 mmole). The reaction mixture was stirred at 0° C for 18 hours or until all of the starting material was consumed as determined by thin layer chromatography on silica gel. When complete, the reaction mixture was washed with water, saturated aqueous sodium bicarbonate solution and saturated aqueous sodium chloride solution. The methylene chloride solution was dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford 11-(N-piperidyl)undecane-1-(p-toluene)sulfonate as a viscous oil (15.81 g., 92.1% yield). ^{1}H-NMR (200 MHz., $CDCl_3$) d = 1.10-1.75 ppm, m, 24H; 2.15-2.65, m, 6H; 2.46, s, 3H; 4.01, t, J=6.4 Hz., 2H; 7.35, d, J=8.3 Hz., 2H; 7.80, d, J=8.3 Hz., 2H. ^{1}H-NMR (200 MHz., CD_3OD) d = 1.10-1.80 ppm, m, 24H; 2.10-2.70, m, 6H; 2.46, s, 3H; 4.01, t, J=6.2 Hz, 2H; 7.44, d, J=8.2 Hz, 2H; 7.78, d, J=8.2 Hz., 2H. IR(neat) 2925, 2880, 2800, 2760, 1610, 1450, 1360, 1175, 1100, 960, 840, 670 cm^{-1}.

B. Polymerization of 11-(N-piperidyl)undecane-1-(p-toluene) sulfonate

This polymerization may be carried out by any method one skilled in the art considers appropriate. Two specific methods of polymerization were used.

1. Self-condensation: On standing over a period of 1-4 weeks, the above monomer polymerizes at room temperature without any added catalyst to form the water soluble polymeric quaternary ammonium salt: poly (11-piperidinium undecane p-toluenesulfonate). m.p. 95-106° C.

2. Heated Self-condensation: It was found that heating a freshly prepared sample of the above monomer speeded up the polymerization process. An NMR analysis of a sample that was heated at 50-60° C for 4 hours showed that it polymerized as quickly as that of a sample stored at room temperature for 3 days. When this heated sample was further heated for an additional 24 hours, it was found by NMR analysis to have almost completely polymerized.

The average change length was found to be 7.

C. Microbicidal activity of poly (11-(N-piperidyl)undecane-1-(p-toluene) sulfonate) compared to commercially available microbicides

The poly 11-(N-piperidyl)undecane-1-(p-toluene) sulfonate exhibits unexpected outstanding biocidal efficacy in complex media in the secondary MIC/SOK test (4-16 ppm range). In a side-by-side test against commercially available quat compounds, poly 11-(N-piperidyl)undecane-1-(p-toluene) sulfonate maintained superior efficacy in the complex media (triptocase soy broth). Especially noteworthy is the Total Kill Test data for of the polymer of the invention and the fact that it is not inactivated by the presence of organic media. In none of the commercially available quats is the nitrogen atom part of a ring.

Table 1

MIC MICROBICIDE TEST DATA (ppm)								
Quat	Total Kill Test	(G-) PSFL	(G-) PSAE	(G-) ECOL	(G+) SAUR	(F) (F) ANIG	APUL	Modified Total Kill
Example 1 (Invention)	4	4	16	8	4	16	4	8
Comparative A	63	>250	250	250	>250	250	>250	
Comparative B	16	1	8	8	1	4	8	
Comparative C	16	1	63	16	2	4	1	

Comparative A = Busan 77™ poly[oxyethylene (dimethyliminio) ethylene (dimethyliminio) ethylenedichloride

Comparative B = Hyamine 1600™ alkyl dimethylbenzyl ammonium chloride

Comparative C = Hyamine 3500™ alkyl dimethylbenzyl ammonium chloride

Invention = Poly 11-(N-piperidyl)undecane-1-(p-toluene) sulfonate

Example 2

Following the procedure of Examples 1 A and B except using 12-bromododecanol instead of 11-bromoundecanol, polymer 2 was prepared.

Example 3

Following the procedure of Examples 1 A and B except using phenylsulfonyl chloride instead of p-toluene sulfonyl chloride, polymer 3 was prepared.

Example 4

Following the procedure of Examples 1 A and B except using p-nitrophenyl sulfonyl chloride instead of p-toluene sulfonyl chloride, polymer 4 was prepared.

Example 5

Following the procedure of Examples 1 A and B except using methane sulfonyl chloride, monomer 5 in crystalline form according to formula IV was prepared.

Example 6

Following the procedure of Examples 1 A and B except using p-chlorophenyl sulfonyl chloride instead of p-toluene sulfonyl chloride, polymer 6 was prepared.

Example 7

Following the procedure of Examples 1 A and B except using hexamethylene imine instead of piperidine, polymer 7 was prepared.

Example 8

Following the procedure of Examples 1 A and B except using pyrrolidine instead of piperidine, polymer 8 was prepared.

Example 9

Following the procedure of Examples 1 A and B except using 12-bromododecanol was used instead of 11-bromoundecanol and hexamethylene imine instead of piperidine, polymer 9 was prepared.

Example 10

Following the procedure of Examples 1 A and B except using 12-bromododecanol and pyrrolidine, polymer 10 was prepared.

Example 11

Following the procedure of Examples 1 A and B except using 12-bromododecanol, pyrrolidine, and phenylsulfonylchloride, polymer 11 was prepared.

Example 12

Following the procedure of Examples 1 A and B except using 12-bromododecanol, hexamethylene imine, and phenylsulfonyl chloride, polymer 12 was prepared.

Example 13

Following the procedure of Examples 1 A and B except using morpholine instead of piperidine, polymer 13 was prepared.

Example 14

The polymers or monomer of Examples 2 to 13 were tested with the results reported in Table 2.

TABLE 2

Test * Example	MIC(ppm)						Total Kill Test (ppm) 4 hrs	Modified Total Kill 10 min results
	Psae	Ecol	Saur	Anig	Apul	Chlor	Psae	
2	63	4	4	4	1	0.5	>250	16
3	16	8	4	8	4	<0.12	-8	8
4	>250	>250	8	32	16	<0.12	>250	>500
5	>250	>250	>250	250	125	>250	>250	>500
6	16	16	63	16	8	250	8	8
7	32	16	8	4	0.5	<0.12	16	16
8	16	8	16	4	0.25	0.25	16	8
9	32	8	4	4	0.5	0.5	125	32
10	4	4	2	1	1	8	32	8
11	4	4	2	4	2	2	16	8
12	63	16	8	16	8	8	250	16
13	>250	>250	63	63	16	-	16	-

*to kill 2.2 x 10^4 CFU in 10min.

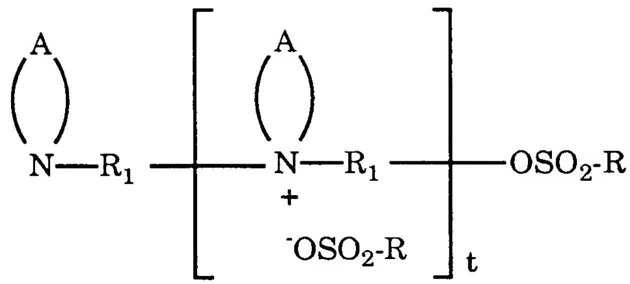
Example 15

SOK for Examples 1 and 11 were measured with the following results in log/3 min. against Psae, Saur, and Schlo using 100 ppm of test compound.

SOK			
Example	Psae	Saur	Schlo
1	4	2	2
11	6	4	5

Claims

1. Compound of the formula (V)



(V)

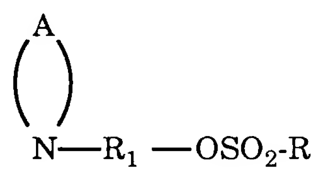
wherein R is $(C_1\text{-}C_{20})$alkyl, $(C_1\text{-}C_{20})$cycloalkyl, or $(C_6\text{-}C_{20})$aryl, aralkyl or alkaryl each optionally substituted on the aryl portion with one or more of halo, nitro, $(C_1\text{-}C_4)$alkyl, or cyano;

A is $(CH_2)_p$, $(CH_2)_q\text{-O-}(CH_2)_r$, or $(CH_2)_q\text{-S-}(CH_2)_r$,

wherein p = 2 to 8, q = 1 to 8, and r = 1 to 8;

R_1 = $\text{-}(CH_2)_m\text{-}$, $\text{-}(CH_2CH_2\text{-O})_n\text{-}CH_2CH_2\text{-}$, or $\text{-}(CH_2CH_2CH_2\text{-O})_n\text{-}CH_2CH_2CH_2\text{-}$ where m is from 7 to 24 and n is from 1 to 10; and t is from 1 to 100.

2. Compound of the formula (IV)



(IV)

wherein A, R, and R_1 are as defined in claim 1.

3. Compound according to claim 1 or 2 wherein t if present is from 4 to 10, and/or m is from 10 to 16, and/or n is from 2 to 5.

4. Compound according to any preceding claim wherein R_1 = $(CH_2)_m$ in which m = 11 or 12, or $(CH_2CH_2\text{-O})_n\text{-}CH_2CH_2$ in which n = 3 or 4, or $(CH_2CH_2CH_2\text{-O})_n\text{-}CH_2CH_2CH_2$ in which n = 2 or 3.

5. Compound according to any preceding claim wherein A = $(CH_2)_p$ and p = 4, 5 or 6.

6. Compound according to any preceding claim wherein R is o-toluene, phenyl, p-toluene, p-chlorophenyl, p-nitrophenyl, or methyl.

7. Compound according to any of claims 1, 2 or 6 wherein

is piperidine, pyrrolidine, or hexamethyleneimine.

8. Compound comprising the product of polymerization of a compound of the formula (IV) as defined in

any of claims 2 to 7.

9. Composition comprising a compound as defined in any preceding claim and a pharmaceutically or agronomically acceptable carrier, or a cosmetic agent, a cutting oil, a soap or synthetic detergent, a stabilizer, a solvent or a film forming material.

10. Composition according to claim 9 wherein the solvent comprises EDTA or sodium dodecyl alcohol.

11. Method of preventing or inhibiting the growth of bacteria, fungi or algae in a locus susceptible or subject to contamination thereby, comprising incorporating into or onto the locus, in an amount effective to adversely affect said growth, a compound or composition according to any preceding claim.

12. Method according to claim 11 wherein said locus is a plant, and the growth being controlled is that of the genus *xanthomonas*.

13. Use of a compound or composition according to any of claims 1 to 10 as a microbicide.

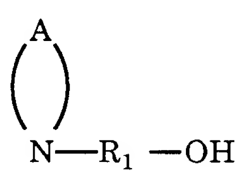
14. Process for producing a compound of the formula (IV) as defined in any of claims 2 to 7, comprising reacting a monoalcohol of the formula

$X\text{-}R_1\text{-}OH$ (I)

wherein R_1 = $-(CH_2)_m-$, $-(CH_2CH_2\text{-}O)_n\text{-}CH_2CH_2-$, or $-(CH_2CH_2CH_2\text{-}O)_n\text{-}CH_2CH_2CH_2-$ in which m = 7 to 24, n = 1 to 10, and wherein X is a leaving group, preferably being Br, Cl, or OSO_2R in which R is alkyl, cycloalkyl, aryl, substituted aryl, alkaryl or aralkyl,
with a molar excess of secondary ring amine of the formula

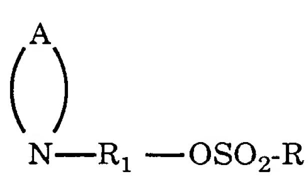
(II)

wherein A is as defined in claim 1 or 5,
to form a compound of the formula



(III)

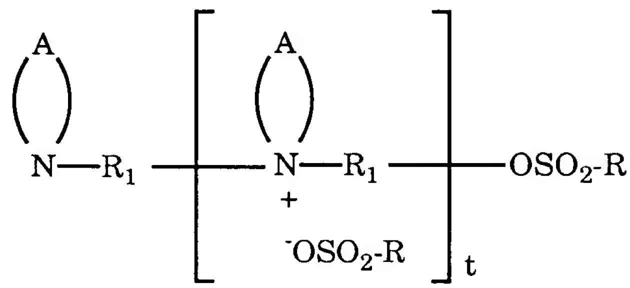
and reacting (III) with $X'SO_2R$ wherein R is as defined in claim 1 or 6 and wherein X' is Cl or Br, to produce a monomer of the formula



(IV)

15. Process for producing a compound of the formula (V) as defined in any of claims 1 or 3 to 7,

comprising polymerizing a monomer (IV) produced according to claim 11 to produce a polymer of the formula



(V)

wherein t is from 1 to 100.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 31 2062

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 569 992 (P.M. QUINLAN) -----		C07D295/088 A01N41/04 C08G73/02
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07D C08G A01N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06 APRIL 1992	PAUWELS G.R.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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